Proceedings of IMECE2002
ASME International Mechanical Engineering Congress & Exposition
November 17-22, 2002, New Orleans, Louisiana

IMECE2002-33728

PREPARATION OF NANOCRYSTALLINE TITANIUM SILICIDE POWDER AND ITS CONSOLIDATION USING SODIUM SILICATE

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ABSTRACT

Statistical design of experiments was employed to assess the effect of mechanical alloying variables and the chemical binder (sodium silicate) percentage on the crystallite size of mechanical alloyed titanium silicide powder and the microhardness of samples consolidated by chemical bonding. The results indicate that mechanical alloying the powder with higher milling time, higher milling speed and lower ball-to-powder ratio and consolidating with 20% sodium silicate gives a combination of fine crystallite size and good microhardness in the compact.

INTRODUCTION

Nanostructured materials have a significant fraction of the total atoms at their grain boundaries [1], as their structure falls in between those of polycrystalline materials and amorphous materials. In polycrystalline materials most atoms are present within the grains and the grain boundaries consist of relatively few atoms. In contrast, amorphous materials do not have grains or boundaries. For this reason, the behavior of nanocrystalline materials is quite different from the behavior of conventional polycrystalline materials or amorphous materials. Of particular interest to mechanical engineers is the fact that nanostructured materials tend to have much greater hardness than conventional polycrystalline materials and also possess considerable high temperature ductility.

While the techniques for producing nanostructured materials as thin films have been relatively well established [2], those for making bulky nanostructured products have received relatively little attention. Conventional sintering of a nanostructured powder would lead to significant grain coarsening and reversal to polycrystalline form. Attention therefore should be paid to the preservation of the nanostructure after consolidation into bulk. Some successful attempts have been made in this direction by employing self-propagating high temperature synthesis (SHS) [3] but there is need for investigating alternative routes for consolidation that ensure preservation of the nanostructure. The first author is the leader of several investigations looking into the possibility of employing the Equal Channel Angular Extrusion (ECAE) process or chemical bonding for this purpose. It has already been demonstrated that nanostructured titanium disilicide billets can be successfully produced by subjecting mechanical alloyed (nanostructured) powder to ECAE [4]. In the present paper, the results of an investigation involving chemical bonding consolidation for producing titanium silicide (Ti_5Si_3) compacts will be presented and discussed.

Silicides and silicide matrix composites involving titanium and molybdenum are considered as advanced high temperature materials. From the mechanical engineer's viewpoint, synthesis of nanostructured forms of these silicides would pave way for further improvement in the high temperature behavior as the hardness and the high temperature ductility of the nanostructured forms are much greater. With this in view, the present authors conducted an investigation involving the consolidation of nanostructured titanium silicide powder. The powder was first mechanical alloyed (MA) to a fine size using an attritor, which is a high-energy ball mill. The fine powder was then consolidated using chemical bonding.

MECHANICAL ALLOYING

This process was originally developed by Benjamin [5] for producing oxide dispersion strengthened superalloys, but has since been used by many investigators to produce fine-scale powder. The attritor is popular equipment for mechanical alloying and consists of a vertical shaft with radial arms rotating in a chamber. The material to be milled is placed in the chamber along with the grinding balls made of hard materials. The milling is usually performed in an inert atmosphere of argon.

CHEMICAL BONDING OF CERAMICS

In this technique, the MA powder is mixed with a suitable chemical binder and then cured and fired for short times at

reasonably low temperatures, to ensure that overheating does not destroy the nanocrystalline structure. The binder can be a liquid or a solid that forms a bridge, film or matrix filler or one that creates bonds by chemical reaction [6]. In the latter case, a coat or film is formed around the ceramic particles and the interface is transformed to an amorphous state upon curing and firing after a short heat treatment. For example the binder polycarbosilane (Allyl Hydridopolycarbosilane-AHPCS) belongs to this category. However, it is possible to sodium silicate to depend upon one or more of the three mechanisms noted earlier, to achieve bonding properties, depending upon the material to be bonded and the Na_2O/SiO_2 ratio. This paper deals with the use of Na_2SiO_3 as the binder. In a separate paper the results of studies using polycarbosilane (AHPCS) will be presented and discussed [7].

EXPERIMENTAL

Factorial design of experiments [8] is capable of providing information about the effects of variables and their interactions upon the properties of interest with relatively few experiments. Therefore this technique was employed to determine the effects of the three important attritor (MA) variables namely, the milling time, the milling speed and the ball-to-powder ratio, on the crystallite size of the milled (MA) powder and the microhardness of the powder compacts made by the chemical consolidation process. The upper (+1) and the lower (-1) levels for the experimental design matrix were chosen as shown in Table 1. These were mainly based upon the operating limits of the attritor available with the authors.

Table 1. Levels of MA variables

Variable	Upper level (+1)	Lower level (-1)
Milling time (X_1)	40 hr	10 hr
Milling speed (X_2)	500 rpm	150 rpm
Ball-to-powder ratio (X_3)	30:1	10:1

Based on 2^3 matrix, the powder batches were milled according to the combinations shown in the first three columns of Table 2. Each combination was repeated twice to assure the repeatability of the results. Commercial titanium silicide (powder) was purchased in one lot and martensitic stainless steel balls of 3 mm diameter were used for grinding.

The milled powder was subjected to X-ray diffraction and the patterns (typical pattern shown in Fig.1) were analyzed to determine the crystallite size using Scherrer's [9] formula. The principle of this method depends on the fact that there is broadening of X-ray diffraction peak as the crystallite size decreases and therefore the Bragg angle range at half-maximum height is a measure of the crystallite size. Each batch of powder was then mixed with chosen percentages (15%, 20% and 25% by volume) of the binder and made into cylindrical cured compacts in a laboratory specimen mounting press. The microhardness value of each compact was measured after curing at 800 C for 2 hr, using a Vickers indentation tester and then each compact was fired in a muffle furnace at 1200 C for one hour. The Vickers hardness of the fired samples was again measured.

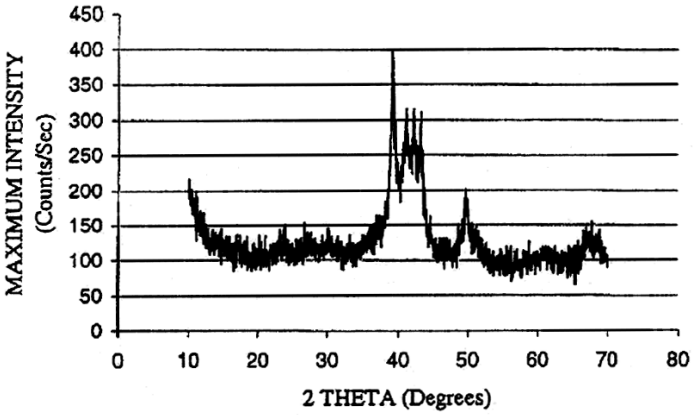

Fig. 1. Typical X-ray diffraction pattern of nanostructured titanium silicide

RESULTS

In Table-2 are shown the crystallite size and the microhardness of each of the eight combinations of the MA variables.

Table 2. Test matrix and Crystallite size

Milling time (X_1)	Milling speed (X_2)	Ball-to-powder ratio (X_3)	Average Crystallite size (CS) nm
+1	+1	+1	9.6
+1	-1	+1	9.4
+1	+1	-1	9.5
+1	-1	-1	11.7
-1	+1	+1	16.7
-1	-1	+1	16.4
-1	+1	-1	2.5
-1	-1	-1	1.7

The regression equations to be derived from the above table are of the form:

$$Y(X_1,X_2,X_3) = a_0+a_1X_1+a_2X_2+a_3X_3+a_{12}X_1X_2+a_{23}X_2X_3+a_{31}X_3X_1+ a_{123}X_1X_2X_3 \quad (1)$$

where,

$a_0=\Sigma(Y/N)$, $a_1=\Sigma(YX_1/N)$, $a_2=\Sigma(YX_2/N)$, $a_3=\Sigma(YX_3/N)$, $a_{12}=\Sigma(YX_1X_2/N)$, $a_{23}=\Sigma(YX_2X_3/N)$, $a_{31}=\Sigma(YX_3X_1/N)$ and $a_{123}=\Sigma(YX_1X_2X_3/N)$.

Here, Y = crystallite size (CS) or microhardness (MH).

The nonlinear regression equation with interaction of coefficients was developed because it was found by standard statistical procedures [10] that the simpler linear equation was statistically inadequate.

The regression equation obtained for the crystallite size was:

$$CS\ (nm) = 9.6 + 0.3X_1 - 0.1X_2 + 3.3X_3 - 0.4X_1X_2 + 0.2X_2X_3 - 3.9\ X_3X_1 + 0.3X_1X_2X_3 \quad (2)$$

It is clear from the regression equation that a negative (lower) value of the ball-to-powder ratio has a strong tendency to reduce the crystallite size. Also the interaction among the variables is such that positive (higher) values of the other two variables bring about significant reduction in the crystallite size. The analysis of variance, shown in the Appendix confirms these observations.

Table 3 shows the microhardness (average of 10 measurements per sample) values of the MA powder mixed with different proportions of polycarbosilane, both in the cured and fired conditions.

Table 3. Microhardness of Titanium Silicide bonded with Sodium Silicate

Milling time X_1	Milling speed X_2	Ball-to-powder ratio X_3	Microhardness values (VHN)					
			After curing (Binder percentage)			After firing (Binder percentage)		
Combination			15	20	25	15	20	25
+1	+1	+1	563	602	573	575	558	564
+1	-1	+1	787	754	575	791	713	586
+1	+1	-1	602	606	607	686	597	485
+1	-1	-1	694	621	537	753	658	567
-1	+1	+1	616	648	681	728	790	633
-1	-1	+1	576	702	594	653	616	563
-1	+1	-1	718	663	628	792	763	627
-1	-1	-1	502	457	399	561	498	441

The regression equations for microhardness values for fired compacts derived from the above data are:

$$MH\ (15\%\ SS) = 692 + 9X_1 + 3X_2 - 6X_3 - 74X_1X_2 - 38X_2X_3 - 13X_3X_1 + X_1X_2X_3 \quad (3)$$

$$MH\ (20\%\ SS) = 649 - 18X_1 + 28X_2 + 20X_3 - 82X_1X_2 - 23X_2X_3 - 16X_3X_1 \quad (4)$$

$$MH\ (25\%\ SS) = 558 - 8X_1 + 19X_2 + 28X_3 - 45X_1X_2 - 7X_2X_3 - 4X_3X_1 + 22X_1X_2X_3 \quad (5)$$

It is evident from Table 3 that there is no significant change in microhardness after firing as compared to that after curing. Also, in general, the microhardness tends to get reduced as the binder percentage increases. However, at the lowest binder percentage (15%) the distribution of the powder in the binder was found to be rather non-uniform. With the other two percentages the distribution was more uniform. As stated earlier, the microhardness of samples with 20% binder was in general better than that at 25%. The best microhardness with 20% binder was obtained under the combination (-1,+1,-1). Reference to Table 2 also indicates that under this combination, the crystallite size is relatively large. On the other hand, under the combination –1,+1,-1, the microhardness is reasonably high and the crystallite size is small. The difficulty with this combination, however was that the fired compacts showed craze cracking, commonly caused by brittleness. As shown in Table 3, the combination (+1,-1,+1) shows the next best microhardness, but the difficulty with this combination was that the powder yield after mechanical alloying was very low, in common with the combinations involving lower milling speed. Based on these considerations, it was concluded by the authors that the combination (+1,+1,-1), that is higher milling time, higher milling speed and lower ball-to-powder ratio, that gave crack-free compacts with reasonably fine crystallite size and reasonably good microhardness was the best combination for processing prior to mixing with 20% sodium silicate, curing and firing. The regression equation (4) does indicate that a higher milling time and lower ball-to-powder ratio tend to decrease the microhardness, but the reduction is somewhat offset by the positive effect of their interaction.

SUMMARY AND CONCLUSIONS

Statistical design of experiments was employed to determine the effects of three mechanical alloying (MA) variables namely, the milling time, the milling speed and the ball-to-powder ratio on the crystallite size and the microhardness of titanium silicide, chemically bonded using sodium silicate. The results indicate that crack-free compact with reasonably fine crystallite size in MA powder and reasonably good microhardness of compacts is obtained under the MA combination of higher milling time, higher milling speed and lower ball-to-powder ratio, when chemically bonded by mixing the milled powder with 20% by weight of sodium silicate and subjecting the mixture to curing and firing.

ACKNOWLEDGEMENT

This work was performed with financial support provided by the Texas Higher Education Coordinating Board under the Advanced Technology Program-1999.

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Malur N. Srinivasan, Ph.D., P.E., is Professor and Chair of the Department of Mechanical Engineering of Lamar University in Beaumont, Texas. He has specialized in the area of Materials Processing and has over 110 publications in refereed journals and conference publications. He has over thirty-five years experience in teaching mechanical engineering courses. S. Aripaka and K. Keshoju will graduate from Lamar University, Beaumont, Texas, each with a Master of Engineering Science degree in mechanical engineering in August 2002.

APPENDIX

Analysis of Variance [11]

$$MEF = (\Sigma Y_i \text{ at high level} - \Sigma Y_i \text{ at low level}) / 4$$

where,

MEF is the main effect factor.

Based on the data in Table 2 the MEF values work out to the following:

Crystallite size

$MEF_{milling\ time} = 0.73$
$MEF_{milling\ speed} = -0.23$
$MEF_{ball\text{-}to\text{-}powder\ ratio} = 6.68$
$MEF_{mt.ms} = -0.78$
$MEF_{ms.bp} = +0.48$
$MEF_{bp.mt} = -7.78$
$MEF_{error} = 0.73$
Total sum of squares = 213.9
Sum of squares for milling time = 1.06
Sum of squares for milling speed = 0.10
Sum of squares for ball/powder ratio = 89.25
Sum of squares for (mt x ms) = 1.22
Sum of squares for (msxbp) = 0.46
Sum of squares for (bpxmt) = 121.1
Sum of squares of error = 213.9-213.2 = 0.7

F-test results:

$F_{milling\ time} = 1.06/0.7 = 1.51$
$F_{milling\ speed} = 0.1/0.7 = 0.14$
$F_{bp\ ratio} = 89.25/0.7 = 127.5$
$F_{mtxms} = 1.22/0.7 = 1.74$
$F_{msxbp} = 0.46/0.7 = 0.66$
$F_{bpxmt} = 121.1/0.7 = 173$

The F values are in good relative agreement with the regression equation (2).

Percentage of variance of milling time = 0.17
Percentage of variance of milling speed = -0.28
Percentage of variance of ball/powder ratio = 41.4
Percentage of variance of mt x ms = 0.22
Percentage of variance of ms x bp = -0.11
Percentage of variance of bp x mt = 56.29

Percentage contribution of error = 100-97.69 = 2.31

Thus the analysis of variance indicates that the regression analysis using nonlinear regression equation has given reasonably good results for crystallite size. Similar statement is valid for the equations for microhardness values as well.